University of British Columbia

QUALITATIVE ANALYSIS

SINGLE SALTS

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QUALITATIVE ANALYSIS—SINGLE SALTS

ABBREVIATIONS USED :—

Ppt. = Precipitate.
Sol. = Soluble.
Soln. = Solution.
O. S. = Original Solution.
Insol. = Insoluble.
$\overline{\overline{T}}$ = Tartrate radical ($C_4H_4O_6$)
$\overline{A}$ = Acetate radical ($C_2H_3O_2$)

ANALYTICAL REACTIONS

REACTIONS OF THE METALLIC RADICALS—KATIONS

The metals, kations, are separated, according to their behaviour with certain general reagents, into five principal groups, two of these groups being each further divided into two sub-groups.

The following table shows the analytical classification of the kations :

GROUP	METALS		CHARACTERISTICS OF THE GROUP
I. Hydrochloric Acid Group. Silver Group.	SILVER LEAD MERCURY(OUS)	Ag′ Pb″ Hg′	Metals whose chlorides are insol. in H_2O and dil. HCl.
II. Hydrogen Sulphide Group. Copper and Tin Groups	II. A: COPPER II. A: MERCURY(IC) II. A: LEAD II. A: BISMUTH II. A: CADMIUM II. B: ARSENIC II. B: ANTIMONY II. B: TIN	Cu″ Hg″ Pb″ Bi‴ Cd″ As‴ Sb‴ Sn″	Metals whose chlorides are sol. in H_2O Metals whose sulphides are insol. in dil. HCl. Sulphides of metals under B. are sol. in $(NH_4)_2S_x$.
III. Ammonium Sulphide Group Iron and Zinc Groups	III. A: IRON, Fe″ & Fe‴ III. A: ALUMINUM III. A: CHROMIUM III. B: MANGANESE III. B: ZINC III. B: NICKEL III. B: COBALT	Fe‴ Al‴ Cr‴ Mn″ Zn″ Ni″ Co″	Metals whose chlorides are sol. in H_2O. Metals whose sulphides are sol. in dil. acids. Metals under A are pptd. by NH_4OH in presence of NH_4Cl. Metals except Al and Cr pptd. as sulphides on addition of NH_4Cl, NH_4OH and $(NH_4)2S$. Al and Cr under these conditions pptd. as hydroxides.
IV. Ammonium Carbonate Group. Alkaline Earth Group.	BARIUM STRONTIUM CALCIUM MAGNESIUM	Ba″ Sr″ Ca″ Mg″	Metals whose chlorides are sol. in H_2O. Metals whose sulphides are sol. in dil. acids and in alkalies. Metals whose hydroxides are not pptd. in presence of NH_4Cl. Metals pptd. by $(NH_4)_2CO_3$ (in presence of NH_4Cl.) as *carbonates*.
V. Alkali Group	POTASSIUM SODIUM AMMONIUM	K′ Na′ NH_4′	Chlorides, sulphides, hydroxides, and carbonates of these are sol. in water. The members of this group have no distinctive group reagent.

The reactions of **each** substance must be written out as in the study of lead, **i. e.,** a short descriptive account of each reaction must be given, **followed by the equation** representing the chemical change.

GROUP I.

Group Reagent, dil. HCl. — Pb, Hg', Ag.

LEAD

1. To a small portion of the clear soln. of lead nitrate, added dilute hydrochloric acid; a white precipitate (ppt.) of lead chloride was thrown down. The ppt. was sol. in hot water, and in a large quantity of cold water. Addition of ammonium hydroxide had no apparent effect on the ppt.

Eq. $Pb(NO_3)_2 + 2\ HCl = PbCl_2 + 2\ HNO_3$
Lead Nitrate + Hydrochloric Acid = Lead Chloride + Nitric Acid

2. Added hydrogen sulphide solution to a small portion of lead nitrate solution; a black ppt. of lead sulphide was thrown down. The ppt. was insol. in dil. HCl.

Eq. $Pb(NO_3)_2 + H_2S = PbS + 2\ HNO_3$
Lead Nitrate + Sulphuretted Hydrogen = Lead Sulphide + Nitric Acid

3. A solution of sodium hydroxide when added to lead nitrate produced an immediate white ppt. of lead hydroxide. This ppt. dissolved on adding excess of the alkali.

Eq. (1) $Pb(NO_3)_2 + 2\ NaOH = Pb(OH)_2 + 2\ NaNO_3$
Lead Nitrate + Sodium Hydroxide = Lead Hydroxide + Sodium Nitrate

(2) $Pb(OH)_2 + 2\ NaOH = Pb(ONa)_2 + 2\ H_2O$
Lead Hydroxide + Sodium Hydroxide = Sodium Plumbite + Water

4. Addition of dil. sulphuric acid to lead nitrate soln. gave a white ppt. of lead sulphate.

Eq. $Pb(NO_3)_2 + H_2SO_4 = Pb\ SO_4 + 2\ HNO_3$
Lead Nitrate + Sulphuric Acid = Lead Sulphate + Nitric Acid

SILVER

1. HCl. White ppt., AgCl.
This ppt. on shaking or warming becomes curdy. Allow the ppt. to subside, pour off the supernatant fluid, and determine the solubility of separate portions of the ppt. in (1) cold H_2O, (2) hot H_2O, (3) NH_4OH, (forms $[Ag\ (NH_3)_2]\ Cl$).

2. NaOH. Dark brown ppt., Ag_2O.
$2\ NaOH + 2\ AgNO_3 = Ag_2O + 2\ NaNO_3 + H_2O$.

3. NH_4OH. Dark brown ppt., Ag_2O.
Note that this ppt. disappears on addition of NH_4OH in excess.

4. H_2S. Black ppt., Ag_2S, insol. in dil. HCl.

1. HCl.—Observe the ppt. of white HgCl on addition of this reagent. Allow to subside and divide the ppt. into 3 parts. Treat one portion with cold water, another with hot water, and the third with NH_4OH; the last reagent changes the HgCl to a mixture of white NH_2HgCl, Mercuro-Ammonium Chloride, and black Hg.

$$2\ NH_4OH + 2\ HgCl = HgNH_2Cl + Hg. + NH_4Cl + 2\ H_2O.$$

2. NaOH. Black ppt., Hg_2O.

$$2\ HgNO_3 + 2\ NaOH = Hg_2O + 2\ NaNO_3 + H_2O.$$

3. NH_4OH. Black ppt., insol. in excess of NH_4OH.

4. H_2S. Black ppt., Hg_2S, insol. in dil. HCl.

GROUP II.

Group Reagent, H_2S in dil. acid soln.

The metals of this group are divisible into two sub-groups, viz., Group II A. and Group II B.

GROUP II.A

Hg. (Pb.), Cd, Cu, Bi.—Sulphides of these metals are **insol.** in $(NH_4)_2Sx$.

MERCURY (IC.)

1. HCl. No ppt.
2. NaOH. Produces a yellow ppt. HgO, changed to white on addition of NH_4OH.
3. $SnCl_2$. A white ppt., HgCl, is first produced, rapidly undergoing reduction to Hg (grey). The final ppt. may be either **grey** or **black** according to the strength of the reagent employed.
4. H_2S. On careful addition of this reagent a **white** ppt. is first produced. Further addition of the reagent changes the ppt. to brown or **orange,** and finally to **black** HgS. These colour changes are characteristic of mercuric salts. Note that this black ppt. is insol. in dil. HCl, NaOH, or $(NH_4)_2S_x$

COPPER

1. HCl. No ppt.
2. NaOH. Pale blue ppt., $Cu(OH)_2$, insol. in excess of alkali.
3. NH_4OH. A greenish blue ppt. (basic salt) sol. in excess of NH_4OH to a deep blue soln. (copper ammonium salt, $Cu(NH_3)_4''$ ion).
4. $K_4Fe(CN)_6$. Chocolate coloured $Cu_2Fe(CN)_6$ (copper ferrocyanide) is pptd.
5. H_2S. Black ppt., CuS, insol. in dil. HCl and insol. in $(NH_4)_2S_x$

CADMIUM

1. HCl. No ppt.
2. NH_4OH. White ppt., $Cd(OH)_2$, sol. in excess. (Cadmium ammonium salt $Cd(NH_3)_4''$ ion).
3. $K_4Fe(CN)_6$.—White ppt., $Cd_2Fe(CN)_6$ (Cadmium ferrocyanide).
4. H_2S. Yellow ppt., CdS, insol. in very dil. HCl and insol. in $(NH_4)_2Sx$.

BISMUTH

1. HCl. No ppt. (cf. test 4.)
2. NaOH or NH_4OH. White $Bi(OH)_3$, insol. in excess. Filter off this ppt. and dissolve it in two or three drops dil. HCl. Add a large quantity of H_2O; a white ppt., BiOCl, is formed.
   $$BiCl_3 + 2\ H_2O = [Bi(OH)_2Cl] + 2\ HCl.$$
   $$[Bi(OH)_2Cl] = BiOCl + H_2O.$$
3. H_2S. Black Bi_2S_3 insol. in dil. HCl and insol. in $(NH_4)_2S_x$
4. Addition of a large quantity of water to a soln. of bismuth salt acidulated with HCl throws down BiOCl. Add H_2S water—the ppt. turns black due to the formation of Bi_2S_3.
   $$2\ BiOCl + 3\ H_2S = Bi_2S_3 + 2\ H_2O + 2\ HCl.$$

LEAD

Lead chloride is somewhat soluble in water, consequently the metal cannot be **completely** precipitated by addition of dil. HCl to a solution of a lead salt. Add HCl to a solution of lead nitrate, allow the ppt. ($PbCl_2$) to subside, and pour off the supernatant liquid. Add H_2S water to the latter and note the deposition of black PbS.

GROUP II.B

As, Sb, Sn.—Sulphides of these metals are sol. in $(NH_4)_2Sx$

ARSENIC

1. HCl. No ppt.

2. H_2S. Yellow ppt., As_2S_3 insol. in dil. HCl, sol. in $(NH_4)_2Sx$. $As_2S_3 + 3(NH_4)_2S_x = (3x—5)S + 2(NH_4)_3AsS_4$, (ammonium thio-arsenate).

3. **Reinsch's Test.** Add a few pieces of copper turnings and some HCl to the solution. On boiling, a greyish black deposit of As forms on the surface of the copper. If the copper, with deposit, be carefully dried and then heated in a dry test-tube, minute, white. glittering crystals of As_2O_3 are deposited on the sides of the tube.

ANTIMONY

1. HCl. No ppt. (cf. test 3.)

2. H_2S. Orange ppt., Sb_2S_3, insoluble in dil. HCl, sol. in str. HCl and in $(NH_4)_2S_x$

3. Acid solutions of antimony salts on treatment with water give white ppts., **e.g.:**

$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$

Add H_2S water—ppt. turns orange.

$$2\ SbOCl + 3\ H_2S = Sb_2S_3 + 2\ H_2O + 2\ HCl.$$

TIN (Stannous)

1. HCl. No ppt.

2. H_2S. SnS ppt. (brown) insol. in dil. HCl, sol. in str. HCl and in $(NH_4)_2S_x$ $[(NH_4)_2SnS_3]$.

3. $HgCl_2$. White to grey ppt., HgCl and Hg.

$$2\ HgCl_2 + SnCl_2 = 2\ HgCl + SnCl_4.$$
$$2\ HgCl + SnCl_2 = 2\ Hg + SnCl_4.$$

GROUP III.

Group reagents, NH_4OH, $(NH_4)_2S$, NH_4Cl.

The metals of this group are divided into two sub-groups, viz., Group III.A. and Group III.B.

GROUP III.A

Group reagent, NH_4OH in presence of NH_4Cl.—Fe″, Fe″′, Al, Cr.

The chlorides of these metals are sol. in water; their sulphides are not pptd. by H_2S in acid soln. and their hydroxides are insol. in NH_4Cl; ammonium sulphide ppts. the metals either as sulphides (Fe″ and Fe″′) or as hydroxides (Al and Cr).

IRON (FERROUS)

1. HCl. No ppt. (Soluble chloride.)

2. H_2S in acid soln. gives no ppt. (sulphide sol. in acid).

3. NH_4OH or NaOH yields dirty green ppt., $Fe(OH)_2$, rapidly undergoing conversion to brownish red $Fe(OH)_3$ on standing in the air. Ferrous hydroxide is insol. in NH_4Cl.

4. $(NH_4)_2S$. Black ppt. FeS.

5. $K_4Fe(CN)_6$, a light blue ppt., $Fe_2Fe(CN)_6$.

6. $K_3Fe(CN)_6$, deep blue ppt., $Fe_3[Fe(CN)_6]_2$. (Turnbull's Blue.)

IRON (FERRIC)

1. HCl. No ppt.

2. H_2S in dil. acid soln. gives no ppt.

3. $(NH_4)_2S$, or H_2S in alkaline soln., gives a black ppt., FeS, as in the case of Fe″ salts, but mixed with free S.
$$2\ FeCl_3 + 3\ (NH_4)_2S = 2\ FeS + 6\ NH_4Cl + S.$$

4. NH_4OH. Reddish brown ppt., $Fe(OH)_3$, insol. in excess.

5. $K_4Fe(CN)_6$. Dark blue ppt. Prussian blue, $Fe_4[Fe(CN)_6]_3$.

6. $K_3Fe(CN)_6$. Reddish-brown coloration.

7. NH_4CNS. Deep blood-red coloration, $Fe(CNS)_3$.

ALUMINUM.

1. HCl. No ppt.

2. H_2S. In acid soln., no ppt.

3. NH_4OH or $(NH_4)_2S$. White gelatinous ppt. $Al(OH)_3$. The ppt. is sol. in NaOH, but the NaOH soln. gives no ppt. on boiling (compare zinc). Addition of NH_4Cl to the NaOH soln. ppts. $Al(OH)_3$ (compare zinc). $3\ NaOH + Al(OH)_3 = Al(ONa)_3 + 3\ H_2O$. $Al(ONa)_3 + 3\ NH_4Cl + 3\ H_2O = Al(OH)_3 + 3\ NaCl + 3\ NH_4OH$.

4. Dry test. Evaporate a few drops of the soln. to dryness. Moisten residue on a wire with a few drops of $Co(NO_3)_2$ and reheat. Blue mass indicates presence of aluminum.

CHROMIUM

1. HCl. No ppt.

2. H_2S. In dil. acid soln., no ppt.

3. NH_4OH or NaOH or $(NH_4)_2S$. Light green $Cr(OH)_3$ is pptd. in every case. Note the solubility of the ppt. in NaOH; on boiling this soln. $Cr(OH)_3$ is repptd. $Cr(OH)_3$ is insol. in NH_4Cl.

4. Evaporate a few drops of the soln. to dryness on a crucible lid. Add a little KNO_3 together with some Na_2CO_3 and heat this mixture in the Bunsen flame. Yellow mass (chromates of Na and K). Dissolve the yellow mass in water, acidify with acetic acid, boil and add $Pb\overline{A}_2$, yellow ppt., $PbCrO_4$.

GROUP III.B

Group reagent $(NH_4)_2S$, in presence of NH_4Cl and NH_4OH.—
Mn, Zn, Ni, Co.

ZINC

1. HCl. No ppt.
2. H_2S. No ppt. of a zinc salt in the presence of a strong acid. In alkaline solutions or in presence of a weak acid, the Zn is completely pptd.
3. NH_4OH. In presence of NH_4Cl, no ppt.
4. NaOH. White ppt. $Zn(OH)_2$. The ppt. is sol. in excess of the reagent. (a) Add water to a portion of the clear soln. and boil.—$Zn(OH)_2$ is repptd. (compare Al.). (b) Add NH_4Cl to another portion of the same soln.—No ppt. (compare Al.). (c) Add H_2S to another portion. White ppt. ZnS.
5. $(NH_4)_2S$. White ppt., ZnS, sol. in dil. acids.
6. Dry test. As for Al. Green mass indicates presence of Zn.

MANGANESE

1. HCl. No ppt.
2. H_2S. In acid soln.—No ppt.
3. NH_4OH. In presence of NH_4Cl.—No ppt. (On standing, dark brown ppt. forms slowly.)
4. NaOH. White ppt. $Mn(OH)_2$. This ppt. rapidly darkens on standing in the air, yielding a dirty brown ppt.
5. $(NH_4)_2S$. Flesh coloured ppt. MnS.
6. Evaporate a few drops of the soln. to dryness on a crucible lid. Add a little Na_2CO_3 and KNO_3 and heat in the Bunsen flame.—Green mass (manganate). Dissolve in small quantity H_2O. Add few drops HCl.—purple color. MnO_4' ion.

NICKEL

1. HCl. No ppt.
2. H_2S. In acid soln.—No ppt.
3. NaOH. Light green ppt., $Ni(OH)_2$.
4. NH_4OH. Light green ppt., $Ni(OH)_2$, sol. in excess to a violet blue soln. Ppt. is also sol. in NH_4Cl.
5. $(NH_4)_2S$. Black ppt. NiS.

COBALT

1. HCl. No ppt.
2. H_2S. In acid soln.—No ppt.
3. NaOH. Blue ppt. $Co(OH)_2$.
4. NH_4OH. Blue ppt., $Co(OH)_2$, sol. in excess of the reagent, yielding a bluish soln. The ppt. is also sol. in NH_4Cl.
5. $(NH_4)_2S$. Black ppt., CoS.

GROUP IV.

Group Reagent $(NH_4)_2CO_3$ in presence of NH_4OH.—
Ba, Sr, Ca, Mg.

The chlorides and sulphides of these metals are sol. in H_2O. Their hydroxides are not pptd. in presence of NH_4Cl. They are pptd. as carbonates on addition of ammonium carbonate, $(NH_4)_2CO_3$, and NH_4OH.

BARIUM

1. The group reagents of Groups I, II and III, viz., HCl, H_2S, NH_4OH, NH_4Cl and $(NH_4)_2S$, give no ppts. with barium salts.
2. $(NH_4)_2CO_3$. White flocculent ppt., $BaCO_3$, insol. in NH_4Cl.
3. $(NH_4)_2C_2O_4$. White ppt., BaC_2O_4.
4. $CaSO_4$ or H_2SO_4. An immediate white ppt., $BaSO_4$.
5. **Flame Test.** Barium salts impart a **green** coloration to the non-luminous flame of the Bunsen. Acidulate the soln. of the barium salt with HCl, dip a piece of wire in the soln. and hold the wire at the lower outside edge of the Bunsen flame.
6. K_2CrO_4. Yellow ppt., $BaCrO_4$, sol. in HCl, insol. in acetic acid.

STRONTIUM

1. As with barium.
2. $(NH_4)_2CO_3$. White flocculent ppt., $SrCO_3$, insol. in NH_4Cl.
3. $(NH_4)_2C_2O_4$. White ppt., SrC_2O_4.
4. $CaSO_4$. White ppt., $SrSO_4$. This ppt. comes down only on standing or on heating the soln. (Compare barium.)
5. **Flame Test.** Strontium salts acidulated with HCl impart a **bright crimson** colouration to the Bunsen flame. Proceed as with barium.
6. K_2CrO_4. No ppt. or very small light yellow coloured ppt.

CALCIUM

1. As with barium.
2. $(NH_4)_2CO_3$. White ppt., $CaCO_3$, insol. in NH_4Cl.
3. $(NH_4)_2C_2O_4$. White ppt., CaC_2O_4.
4. $CaSO_4$. No ppt.
5. **Flame Test.** Calcium salts acidulated with HCl impart a **brick red** colouration to the Bunsen flame. Proceed as with barium.
6. K_2CrO_4. No ppt.

MAGNESIUM

1. As with barium.

2. NH_4OH. White ppt., $Mg(OH)_2$. A high concentration of NH_4OH necessary to ppt. $Mg(OH)_2$. Add NH_4Cl and observe that the ppt. disappears. Explain.

3. $(NH_4)_2CO_3$ and NH_4OH. White ppt. (only in strong solns.).

4. Add NH_4Cl and NH_4OH to the soln. of the magnesium salt and afterwards Na_2HPO_4.—a white ppt., $MgNH_4PO_4$, is thrown down. In dilute solns. of magnesium salts this ppt. appears only on stirring with a glass rod or on standing.

5. $(NH_4)_2C_2O_4$. White ppt., MgC_2O_4.

6. K_2CrO_4. No ppt.

GROUP V.

K, Na and NH_4.

The chlorides, sulphides, hydroxides, carbonates and phosphates of these metals being soluble in water, addition of any one of the group reagents of Groups I, II, III, IV and V fails to produce a ppt. The members of this group have no specific group reagent and are generally detected by special tests.

POTASSIUM.

1. The group reagents of Groups I, II, III, IV and V give no ppt.

2. $NaHC_4H_4O_6$ ($NaH\overline{T}$), with **vigorous** stirring. White crystalline ppt. $KH\overline{T}$ in **strong** solutions. The ppt. is sol. in much water, hence dilute solns. of potassium salts fail to give the reaction.

3. **Flame Test.** Salts of potassium impart a violet or lilac colouration to the Bunsen flame.

SODIUM

1. As in the case of potassium.

2. $NaH\overline{T}$. No ppt.

3. **Flame Test.** Intense, persistent, golden yellow colouration.

AMMONIUM

1. As for K and Na.

2. $NaH\overline{T}$. White ppt. $NH_4H\overline{T}$ in **strong** solutions; sol. in much water.

3. Add NaOH soln. and heat. NH_3 gas is evolved and may be detected by its characteristic pungent odour, as well as by its action on red litmus papers.

REACTIONS OF THE ACID RADICALS — ANIONS

The non-metallic elements exist in solution, in some cases, as simple anions, but more frequently they are combined with oxygen, or some other elements, to form compound anions—the radicals of acids. These acid radicals cannot be grouped as rigourously as the metallic radicals, but are usually detected by more or less special tests; the following, however, is a classification which is found convenient in the case of simple salts:

The reactions of the anions are commonly spoken of as the reactions of the corresponding acids (or salts); they will, therefore, be listed so here.

(A) Acids which are liberated from their salts by dilute HCl or HNO_3 and partially volatilised (either as the acid itself or as its anhydride). The reaction may be obtained by treating either an aqueous solution of the salt, or the powdered salt itself, with dilute HCl or HNO_3. — H_2CO_3, H_2SO_3, H_2S.

(B) Acids which give a ppt. with $AgNO_3$ in nitric acid solution.

(C) Acids whose salts give no noticeable reaction with dilute HCl or HNO_3, or with $AgNO_3$ in nitric acid solution, but do give such a reaction with concentrated H_2SO_4. To obtain this reaction, the powdered salt is placed in a test-tube in sufficient quantity to fill the hemispherical bottom of the tube, and enough acid is added to cover the powder; if no reaction takes place in the cold, the mixture is carefully warmed. (The acids of the preceding group also give reactions with concentrated H_2SO_4) — HNO_3, $H_2C_2O_4$, $HC_2H_3O_2$, $H_2C_4H_4O_6$.

(D) Acids which do not give noticeable reactions with the above-mentioned reagents.—H_2SO_4, H_3PO_4, H_3BO_3.

GROUP A.

CARBONATES

1. Dil. HCl or HNO_3 added to aqueous sol. or to powdered salt, H_2CO_3, is formed which breaks up into H_2O and CO_2, the latter escaping with effervescence. CO_2 is odourless, and turns lime-water milky.

2. H_2SO_4. Same reaction as under 1.

3. $CaCl_2$, added to aqueous soln. of the salt. White ppt., $CaCO_3$, sol. in HCl.

SULPHITES

1. Dil. HCl or HNO_3, added to aqueous soln. or to powdered salt. H_2SO_3 is formed, which breaks up into H_2O and SO_2, the latter escaping with effervescence. SO_2, odor of burning S, turns filter-paper soaked in soln. of yellow K_2CrO_4 green.

2. H_2SO_4. Same reaction as under 1.

3. Add a little dil. HCl and a piece of Zn to some of the aqueous soln. H_2S is evolved.

$$Zn + 2\ HCl = ZnCl_2 + 2\ H.$$
$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2SO_3.$$
$$6\ H + H_2SO_3 = H_2S + 3\ H_2O.$$

SULPHIDES

1. Dil. HCl or HNO_3, added to aqueous soln. or to powdered salt. H_2S is formed and volatilises; gas turns paper soaked in $Pb\overline{A}_2$ black.

2. H_2SO_4. H_2S (and SO_2) volatilised.

3. $Pb\overline{A}_2$ added to aqueous soln. Black ppt., PbS.

GROUP B.

CHLORIDES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. Pungent fumes of HCl.
3. H_2SO_4 and MnO_2. Greenish yellow fumes of Cl, which bleach moist litmus paper.
4. $AgNO_3$, with aqueous or HNO_3 soln. White ppt. of AgCl, insol. in HNO_3, sol. in NH_4OH.

BROMIDES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. Pungent fumes of HBr, mixed with Br, brown (and SO_2).
3. H_2SO_4 and MnO_2. Brown fumes of Br.
4. $AgNO_3$, with aqueous or HNO_3 soln. Pale yellow ppt. of AgBr, insol. in HNO_3, much less sol. in NH_4OH than AgCl.
5. Cl water liberates Br, soluble in a drop or two of chloroform, turning it brown.

IODIDES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. Pungent fumes I, violet (with SO_2 and H_2S). Solid I crystals often deposit on upper part of test-tube. I turns starch paper blue.
3. H_2SO_4 and MnO_2. Violet fumes of I with characteristics given in test 2.
4. $AgNO_3$, with aqueous or HNO_3 solution. Yellow ppt. of AgI, insol. in HNO_3 and in NH_4OH.
5. Cl water liberates I, soluble in a drop or two of chloroform, turning it violet.

NITRATES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. Odor of HNO_3. On adding Cu, fumes of NO and NO_2 (brown).
3. To a little of the strong aqueous solution of the salt add an equal volume of strong $FeSO_4$ solution, both cold. Allow a small quantity of strong H_2SO_4 to run down the side of the tube so that it sinks below the solution without mixing; a brown ring forms at the contact of the two liquids.
4. $AgNO_3$ with aqueous or HNO_3 soln. No ppt.

ACETATES

1. Dil. HCl or HNO_3. No noticeable reaction (except, possibly, odor of vinegar).

2. H_2SO_4 (conc.) with powdered salt. Odor of vinegar, and mixture darkens in color. If alcohol be added and the mixture warmed, pleasant odor of ethyl acetate.

OXALATES

1. Dil. HCl or HNO_3. No noticeable reaction.

2. H_2SO_4 (conc.) with powdered salt. CO_2 and CO evolved on warming, former turns lime-water milky, and latter burns with blue flame.

3. H_2SO_4 (dil.) and MnO_2. CO_2 evolved on warming. Turns drop of lime-water on rod milky.

TARTRATES

1. Dil. HCl or HNO_3. No noticeable reaction.

2. H_2SO_4 (conc.) with powdered salt. Mixture darkens (chars) on warming, and evolves odor of burnt sugar and of SO_2.

3. KOH and $HC_2H_3O_2$ added to strong aqueous solution. Ppt. of $KH\overline{T}$.

4. $CaCl_2$. Ppt. of $Ca\overline{T}$ in the cold.

GROUP C.

SULPHATES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. No noticeable reaction.
3. $BaCl_2$. White ppt., $BaSO_4$, insol. in HCl or HNO_3.

PHOSPHATES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. No noticeable reaction.
3. $BaCl_2$. White ppt., $Ba_3(PO_4)_2$, sol. in HCl or HNO_3.
4. $(NH_4)_2MoO_4$, in presence of HNO_3. Yellow ppt. (warming may be necessary).
5. $AgNO_3$, in neutral solution. Yellow ppt., Ag_3PO_4, sol. in HNO_3 or in NH_4OH.

BORATES

1. Dil. HCl or HNO_3. No noticeable reaction.
2. H_2SO_4 (conc.) with powdered salt. No noticeable reaction.
3. C_2H_5OH and H_2SO_4. Solution on glass rod burns with green-edged flame.
4. $AgNO_3$, in neutral solution. White ppt., sol. in HNO_3 or in NH_4OH.

UNKNOWN SINGLE SALTS

The material, as submitted for analysis, should be carefully examined and briefly described in the notes.

To dissolve an unknown solid salt, place as much of the powder as can be lifted on a ten-cent piece in a test-tube, add about 2 inches of water, shake and warm. If solution does not take place, add a little HCl and shake and warm again. If solution does not now take place, warm a fresh quantity of the powdered salt with about an inch of strong HCl and then dilute with water. If this does not effect solution, try the same procedure with dilute and then with strong HNO_3.

Notice carefully any peculiar phenomena (effervescence, etc.), that may occur during solution.

The solution obtained as described is called the original solution, O.S.

In testing for acids, it must be carefully kept in mind what acid, if any, has been used in making up the O.S.

The positive reactions obtained are to be expressed wherever possible by equations.

EXAMINATION FOR THE KATION

GROUP I.

Treat a portion of the original soln. with dil. HCl and warm gently. A white ppt. indicates presence of Ag, Pb, or Hg^{ous}. Decant and treat the white ppt. with NH_4OH.

(a) Ppt. dissolves = Ag. Confirm by adding NH_4OH to the O.S., brown ppt., sol. in excess = Ag.

(b) Ppt. truns black = Hg^{ous}. Confirm by adding NaOH to the O.S., black ppt. = Hg^{ous}.

(c) Ppt. is unchanged = Pb. Confirm by adding dil. H_2SO_4 to the O.S., white ppt. = Pb.

GROUP II.

If the original soln. gave no ppt. with HCl, add to this acidulated liquid, H_2S water in excess and warm. A ppt. indicates presence of Hg^{ic}, Bi, Cu, Cd, (Pb), As, Sb, Sn^{ous}. Treat ppt. with $(NH_4)_2S_x$

(A) Ppt. is insoluble. Hg^{ic}, Bi, Cu, Cd, (Pb).

(1) To O.S. add NaOH. Yellow ppt. = Hg^{ic}, Confirm by adding $SnCl_2$ to O.S. Grey or black ppt. = Hg^{ic}, (White ppt. sol. in excess = Pb. Confirm by adding H_2SO_4 to O.S. White ppt. = Pb.)

(2) To O.S. add NH_4OH.

(a) Deep blue soln. = Cu. Confirm by adding $K_4Fe(CN)_6$ to O.S. Chocolate ppt. = Cu.

(b) White ppt. = Bi or Cd.
If soluble in excess = Cd. Confirm: H_2S, yellow ppt.
If insoluble in excess = Bi. Confirm: H_2S, black ppt.

(B) Ppt. is soluble = As, Sb, Sn^{ous}.

(1) H_2S ppt. was yellow = As. Confirm by Reinsch's test.

(2) H_2S ppt. was orange = Sb. Confirm.

(3) H_2S ppt. was brown = Sn^{ous}. Confirm by adding $HgCl_2$, drop by drop, to O.S. White or grey ppt. = Sn .

GROUP III.

If no ppt. is obtained with HCl and H_2S, add to a portion of the O.S. excess of NH_4Cl and NH_4OH.

(A) A ppt. = Fe^{ous}, Fe^{ic}, Al, Cr.

(1) Ppt. was dull green = Fe^{ous}. Confirm by adding $K_3Fe(CN)_6$ to O.S. Deep blue ppt. = Fe^{ous}.

(2) Ppt. was reddish-brown = Fe^{ic}. Confirm by adding $K_4Fe(CN)_6$ to O.S. Deep blue ppt. = Fe^{ic}.

(3) Ppt. was white = Al. Confirm by $Co(NO_3)_2$ test. Blue mass = Al.

(4) Ppt. was bluish-green = Cr. Confirm by fusion test.

(B) No ppt. Add $(NH_4)_2S$ to same soln. A ppt. = Zn, Mn, Ni, Co.

(1) Ppt. was white = Zn. Confirm by $Co(NO_3)_2$ test. Green mass = Zn.

(2) Ppt. was flesh-coloured = Mn. Confirm by fusion test.

(3) Ppt. was black = Ni or Co. Add NaOH to O.S.

(a) Apple-green ppt. = Ni. Confirm.

(b) Pale blue ppt. = Co. Confirm.

GROUP IV.

If no ppt. is obtained with NH_4OH, NH_4Cl, and $(NH_4)_2S$, add to a portion of the O.S. NH_4Cl, NH_4OH and $(NH_4)_2CO_3$. White ppt. indicates presence of Ba, Sr, Ca, or Mg.

To the O.S. add $CaSO_4$:—

(a) Immediate white ppt. = Ba. Confirm by flame test. Green flame = Ba.

(b) Ppt. after some time or on warming = Sr. Confirm by flame test. Crimson red = Sr.

(c) No ppt. = Ca. Confirm by flame test. Brick red = Ca.

(d) No ppt. with $(NH_4)_2$, C_2O_4, add Na_2HPO_4 and NH_4OH. White ppt. = Mg.

GROUP V.

If no ppts. have been obtained with the group reagents already named, make the following tests:—

(a) To O.S. add NaOH, and heat. NH_3 is evolved, recognized by smell and action on red litmus paper = NH_4.

(b) To O.S. (strong) add $NaHT\overline{T}$, and shake vigourously. White crystalline ppt. = K. Confirm by flame test. Lilac flame = K.

(c) Determine flame reaction of O.S. Bright, persistent, golden yellow colouration = Na.

EXAMINATION FOR THE ANION

GROUP A.

To a little of the dry salt, add dilute HCl, warm if no reaction takes place in the cold.—A colourless gas is evolved.

(a) No odor. Confirm by means of a drop of lime-water held on a rod in the gas = H_2CO_3.

(b) Odor of burning sulphur. Confirm by means of a drop of K_2CrO_4 held on a rod in the gas = H_2SO_3.

(c) Disagreeable odor. Confirm by means of PbA_2 test = H_2S.

GROUP B.

Add $AgNO_3$ and HNO_3 to the O.S. White ppt., HCl, HBr or HI. To distinguish between these, treat a little of the dry salt with MnO_2 and H_2SO_4.

GROUP C.

To a little of the dry salt add a few drops of concentrated H_2SO_4 (CARE); warm if no reaction takes place in the cold.—A noticeable reaction takes place.

(a) Odor of HNO_3; on addition of Cu, brown fumes. Confirm by brown ring test = HNO_3.

(b) CO_2 and CO evolved on warming. Confirm by means of H_2SO_4 and MnO_2 = $H_2C_2O_4$.

(c) Odor of vinegar, and salt somewhat charred. Confirm by means of ethyl acetate test = $HC_2H_3O_2$.

(d) Mixture chars and gives odor of burnt sugar:
O.S. (strong) with KOH and $HC_2H_3O_2$, ppt. on stirring. Confirm by means of $CaCl_2$ test = $H_2C_4H_4O_6$.

GROUP D.

To O.S. add $BaCl_2$ and HCl. White ppt. = H_2SO_4.

To O.S. add a few drops of HNO_3 and then $(NH_4)_2MoO_4$. Yellow ppt. immediately, or on warming. Confirm by $AgNO_3$ test = H_3PO_4.

To O.S. add strong H_2SO_4 and a little alcohol, stir with a rod. The solution on the rod, when ignited, burns with a green-edged flame. Confirm by $AgNO_3$ test = H_3BO_3.